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Carbon's Three-Center-Four-Electron Tetrel Bond, Treated Experimentally

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ABSTRACT: Tetrel bonding is the noncovalent interaction of Group IV elements with electron donors. It is a weak, directional interaction that resembles hydrogen and halogen bonding, yet remains barely explored. Herein, we present an experimental investigation of the carbon-centered, three-center four-electron tetrel bond, $[N–C–N]^+$, formed by capturing a carbenium ion with a bidentate Lewis base. NMR-spectroscopic, titration-calorimetric- and reaction-kinetic evidence for the existence and structure of this species is reported. The studied interaction is by far the strongest tetrel bond reported so far, and is discussed in comparison with the analogous halogen bond. The necessity of the involvement of a bidentate Lewis base in its formation is demonstrated by providing spectroscopic and crystallographic evidence that a monodentate Lewis base induces a reaction rather than stabilizing the tetrel bond complex. A vastly decreased Lewis basicity of the bidentate ligand or reduced Lewis acidity of the carbenium ion weakens – or even prohibits – the formation of the tetrel bond complex, whereas synthetic modifications facilitating attractive orbital overlaps promote it. As the geometry of the complex resembles the S_N2 transition state, it provides a model system for the investigation of fundamental reaction mechanisms and chemical bonding theories.

INTRODUCTION

Noncovalent interactions are receiving a vastly increasing interest. Over the past decade, the hydrogen bond has been redefined,[1] and the analogous halogen,[2] pnictogen,[3] chalcogen,[4,5] aearogen[6] and coinage-metal[7] bonds have been categorized[8,9] as either σ-hole[10] or E-bond interactions.[7] These interactions, Z–X···Y, are typically observed between a Lewis base, Y, and a region of positive electrostatic potential on atom X, being an electrophile connected to atom Z, along the extension of the Z–X bond. The stronger the interaction, the shorter and more directional the X–Y and the longer the Z–X bond is. When the Lewis basicity of the atoms Z and Y are closely matched (Z ≈ Y), the central electrophilic atom X is equally shared between them, and accordingly the Z–X and X–Y bonds are equally strong and equally long. These interactions were described as three-center four-electron bonds.[11] With a proton being the electrophilic atom (X = H), this special bond (Y–X–Y) is commonly termed a "low-barrier", a "short" or a "strong" hydrogen bond.[12] The low-barrier N–H–N and O–H–O hydrogen bonds received great interest, as they were proposed to be extra strong – up to ~125 kJ/mol – and accordingly stabilize transition states and intermediates, for example in enzyme-catalyzed reactions.[13,14] Their true nature and geometry, however, remains the subject of intense debates.[15-17] The analogous Y–X–Y halogen bond is static and symmetric both in solutions and in the solid state, and possesses a partial covalent character.[18-23] Whereas conventional halogen bonds, R–X···Y, are up to ~40 kJ/mol energy, the three-center four-electron halogen bonds are significantly stronger, 120-150 kJ/mol.[19,21] Due to its exceptional strength, the three-center N-I-N halogen bond is applicable for stabilization of intricate complex supramolecular complexes, for instance.[24-26] The noncovalent interactions in which tetrel elements, i.e. those belonging to Group IV of the periodic system, act as electrophiles are typically very weak, < 10 kJ/mol.[27] Both computational and experimental evidence is available for the lightest tetrel element, carbon, forming tetrel bonds.[28-30] Complexes possessing a three-center four electron tetrel bond with carbon acting as the electrophilic center correspond to a pentacoordinate configuration[11] that is commonly referred to as an "activated complex" or "transition state". This labile geometry[31] involves a trigonal bipyramidal carbon with three of its substituents situated in one plane, whilst the incoming nucleophile and leaving group are positioned apically in a linear three-center four-electron tetrel bond. Among other reactions, the classical bimolecular nucleophilic substitution (S_N2) passes through this high energy configuration, as discussed in virtually every undergraduate textbook. The carbon tetrel bond has been suggested to play a critical role in directing S_N2 reactions.[32] Because of its fundamental importance, the generation of model compounds allowing the experimental investigation

of this carbon configuration has raised vast interest. All model systems so far explored experimentally are *intra*molecular,[33-40] and possess two intramolecular electron donor functionalities geometrically forced into the apical positions of the electrophilic carbon, trapping it in a (pseudo)pentacoordinate configuration.[34-39,41,42]

By contrast, the investigation of *inter*molecular complexes that require formation of a thermodynamically stable three-center four-electron tetrel bond, allowing dissociation or smooth adjustment of bond distances and angles for a stable geometry, has so far lagged behind. Herein, we present the first *inter*molecular three-center four-electron tetrel bond complex possessing a carbon as the central electrophile, and its investigation in solution.

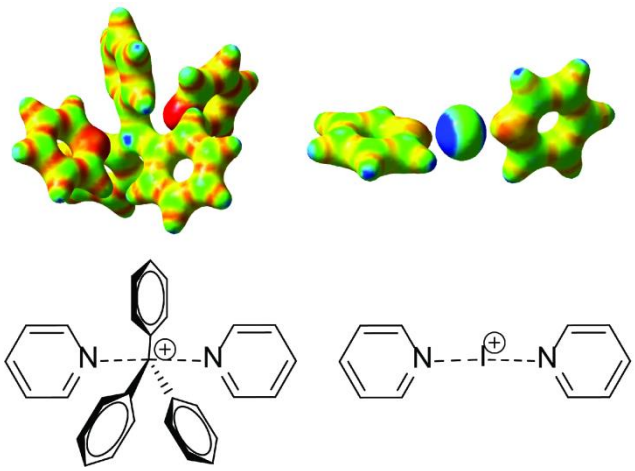


Figure 1. The three-center four-electron bond, $[N\cdots C\cdots N]^+$, of a hypercoordinate carbon (left) resembles the isoelectronic three-center halogen bond, $[N\cdots X\cdots N]^+$ (right). The empty p-orbital of the central atom of both complexes possesses two electrophilic regions (blue) that simultaneously receive electrons from two Lewis bases (red), the nonbonding orbitals of two complexing pyridines. The structures shown are [bis(pyridine)triphenylcarbenium]$^+$ (left) and [bis(pyridine)iodine]$^+$ (right) and are illustrated with their color-coded electrostatic potential mapped on the electron isodensity surface at a contour value of 0.09 electron Bohr^{-3}. The color ramp indicates the most negative potential red (0.3 a.u.) and the most positive potential blue (0.85 a.u.).

Lately, the analogy of the three-center four-electron tetrel bond of carbons[38] to those of the isoelectronic halogen bond, such as that of the central halogen of the triiodide ion, $[I\cdots I\cdots I]^-$,[42,43] and of $[N\cdots X\cdots N]^+$ complexes,[18,19,23] has been recognized.[11,44-47] The three-center halogen bond of $[N\cdots X\cdots N]^+$ complexes is formed by the donation of two unshared electrons of the nitrogens into the 'p–holes', that is the two lobes of the vacant p–orbital of the halogen(I) (Figure 1).[48] These 'p-holes' are analogous to the electron depleted σ–hole that gives rise to the formation of classical halogen, chalcogen, pnictogen and tetrel bonds.[49] Whereas the three-center four-electron halogen bond complexes have been assessed experimentally, the corresponding compounds encompassing three-center four-electron tetrel bonds have so far been studied *in silico*,[41,47] but rarely under standard laboratory conditions in solution.[37,38] The molecular system studied here resembles the one we previously applied for the assessment of the isoelectronic halogen bond.[18,19] Similar to the cationic halogen, X^+, held in position by two N–X halogen bonds, the carbenium carbon, C^+, of **1a-f** (Figures 1 and 2) has an empty p-orbital capable of simultaneously forming two N–C bonds upon overlapping with the nonbonding orbital of the two nitrogen donors that are positioned at optimal distance and in an ideal orientation provided by **2a-c**. This orbital overlap is expected to yield two bonds possessing a partial covalent character,[19,23,48] The resulting complex (**3a-f**, Figure 2) ought to have a three-center four-electron $[N\cdots C\cdots N]^+$ tetrel bond and a trigonal bipyramidal geometry, analogous to that of the transition state of S_N2.[39] Here, we present the synthesis, solution NMR-spectroscopic, calorimetric, and kinetic investigations of the intermolecular tetrel bond complexes **3.**

RESULTS AND DISCUSSION

Synthesis. 1,2-bis(pyridin-2-ylethynyl)benzenes **2a-c** were synthesized following a published procedure.[21] Pyridine, 4-picoline, **1a** and **1f** were commercially available, whereas **1d** and **1e** were synthesized from their triaryl alcohol and triaryl halide precursors, respectively (Supporting Information).[50] To generate complexes **3a-f (**Figure 2, Table 1), **1a-f** and ligands **2a-c** (1:1) were mixed at room temperature under dry conditions in an NMR tube, using dry CD_2Cl_2 as solvent. For the generation of **5b-c** (Figure 2, Table 1), two equivalents of dry pyridine or picoline were added to the CD_2Cl_2 solution of triphenylcarbenium tetrafluoroborate, **1a**.

Structure elucidation. As ^{15}N NMR has an inherently wide chemical shift range of ~800 ppm, it is expected to provide large, easy-to-detect chemical shift changes upon formation of weak molecular complexes in which a nitrogen acts as a Lewis base.[22,48,51] Accordingly, ~100 ppm ^{15}N NMR coordination shifts, $\Delta\delta^{15}N_{coord}$, have been reported for formation of $[N\cdots I\cdots N]^+$ halogen-bonded complexes.[18,19,21,23] Following literature conventions,[21] $\Delta\delta_{coord}$ is defined as the chemical shift difference of the complex and the free ligand, that is $\Delta\delta_{coord} = \delta_{complex} - \delta_{ligand}$. Because of its proven applicability, ^{15}N NMR was applied here as the primary tool to detect analogous $[N\cdots C\cdots N]^+$ tetrel bond complexes (Table 1). The observation of a single set of ^{15}N NMR signals for **3a-f** suggests the formation of complexes in which the carbenium carbon is equally bound to both Lewis basic nitrogens (Table 1, Figure 3). Accordingly, the ^{15}N NMR chemical shift change observed on the bidentate ligand is accompanied by a large ^{13}C NMR chemical shift change of the carbenium carbon (Table 1) of the interaction partner, thus supporting the formation of a $[N\cdots C\cdots N]^+$ three-center four-electron tetrel bond in **3a-d**, whereas revealing the formation of no, or very weak, complexes for **3e-f**. The observed ^{15}N complexation shifts, $\Delta\delta^{15}N_{coord}$, are comparable in magnitude, yet are somewhat smaller than those observed for the isoelectronic halogen bonded compounds.[19,21-23]

Upon mixing **1a** with 1,2-bis(phenylethynyl)benzene, an analogue of **2c** lacking any Lewis basic nitrogen, no ^{13}C NMR chemical shift alteration on **1a** could be observed (Figure S1, Supporting Information), corroborating that the interaction seen for **3a-f** involves the nitrogens. As an additional control to confirm the involvement of the trityl carbon in the interaction responsible for formation of **3a-f**, the ^{15}N NMR shift of **2c** was measured in the presence of tri-*p*-tolylmethanol. This resulted in no nitrogen chemical shift alteration of **2c** (Figure S2, Supporting Information). The two control experiments confirm that the large $\Delta\delta^{15}N_{coord}$ and $\Delta\delta^{13}C_{coord}$ observed for **3c** cannot be due to moisture-induced decomposition of **1a** and subsequent hydrogen bonding of triphenylmethanol to **2c**.

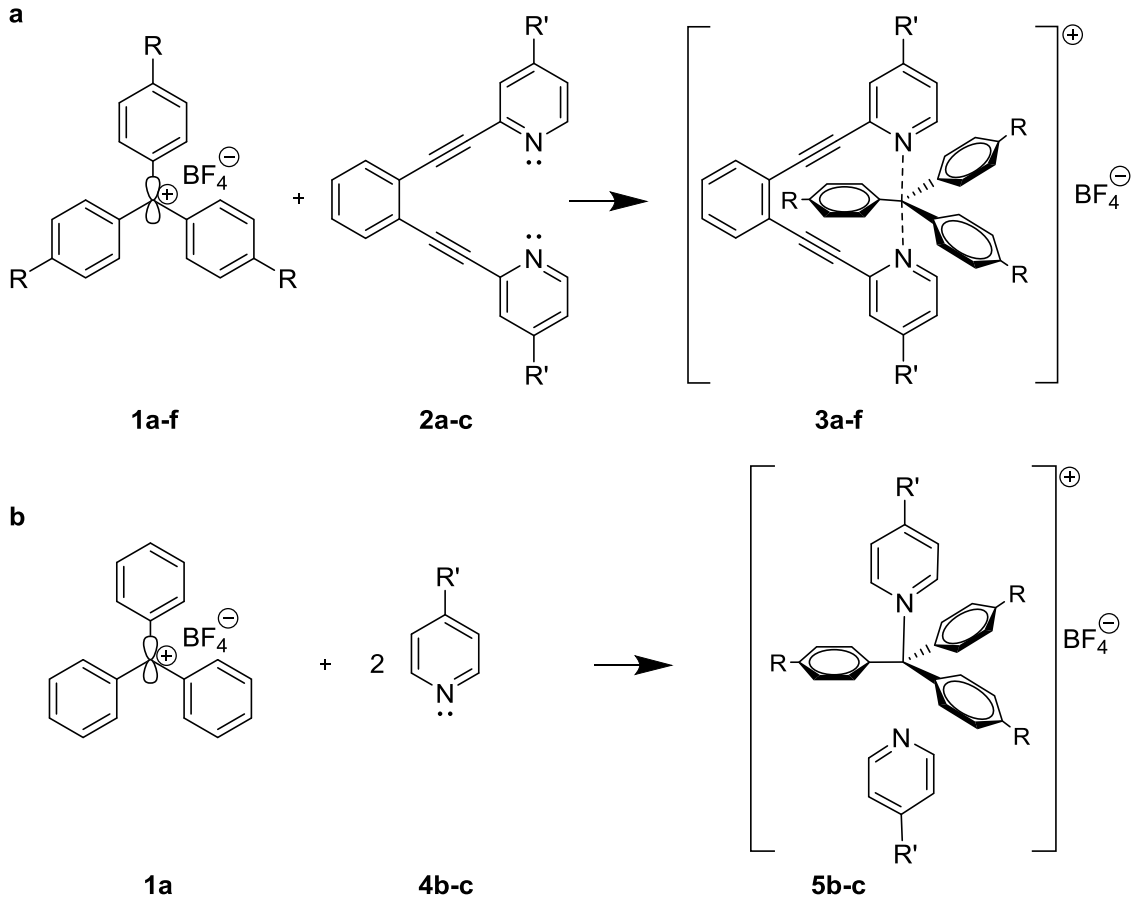
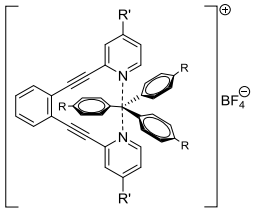


Figure 2. Synthesis of complexes **3a-f** and **5b-c**. For all compounds, R = H (a-c), Me (d), OMe (e), NMe_2 (f), R' = CF_3 (a), Me (b), and H (c-f). Hence, **3a** (**1a+2a**), **3b** (**1a+2b**), **3c** (**1a+2c**), **3d** (**1d+2c**), **3e** (**1e+2c**), **3f** (**1f+2c**), **5b** (**1a+4b**), and **5c** (**1a+4c**). Conditions: The compounds were mixed in dry CD_2Cl_2 at room temperature in an NMR tube. The structure of **3a-f** is not necessarily its preferred conformation.

Table 1. The ^{15}N and ^{13}C NMR Chemical Shifts[a] and Coordination Shifts (ppm) of [N···C···N]$^+$ Tetrel Bond Complexes.

	R, R'	$\delta^{15}N_{ligand}$	$\delta^{15}N_{complex}$	$\Delta\delta^{15}N_{coord}$	$\delta^{13}C_{ligand}$	$\delta^{13}C_{complex}$	$\Delta\,\delta^{13}C_{coord}$
3a (1a+2a)	H, CF_3	-53.4	-81.5	-28.1	211.3	101.1	-110.2
3b (1a+2b)	H, Me	-69.2	-151.2	-82.0	211.3	101.1	-110.2
3c (1a+2c)	H, H	-64.5	-144.0	-79.5	211.3	101.5	-109.8
3d (1d+2c)	Me, H	-64.5	-110.0	-45.5	205.0	82	-123.0
3e (1e+2c)	OMe, H	-64.5	-80.5	-16.0	193.0	193.0	0.0
3f (1f+2c)	NMe_2, H	-64.5	-64.9	0.4	178.7	178.7	0.0
5b (1a+4b)	H, Me	-73.8	-160.3	-86.5	211.3	89.2	-122.1
			-115.5	-41.7			
5c (1a+4c)	H, H	-67.0	-153.3	-86.3	211.3	90.3	-121.0
			-75.8	-8.8			



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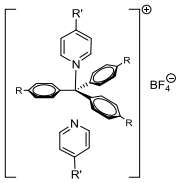

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[a] ^{15}N NMR shifts were referenced to CH_3NO_2 (0 ppm) using a closed capillary.[51]

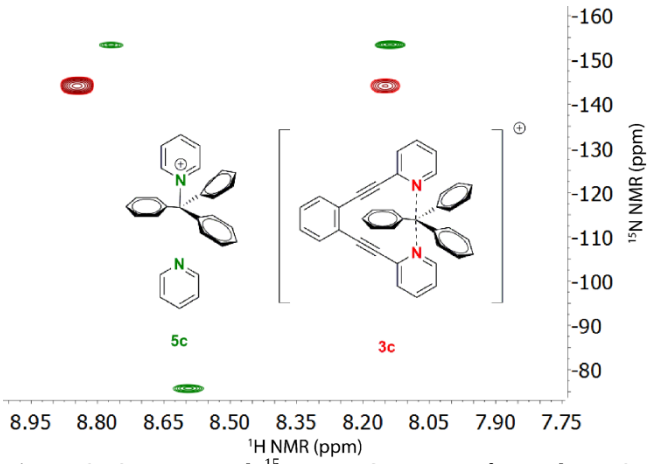

Figure 3. Superimposed ^{15}N HMBC spectra of complexes **3c** (red) and **5c** (green) acquired in CD_2Cl_2 solution at 25 °C. Whereas **3c** shows a single set of ^{15}N NMR signals suggesting equally strong coordination of the carbenium ion to both nitrogens, **5c** has an asymmetric structure with a strongly and a weakly coordinating nitrogen revealed by two sets of signals. Note that the structure drawn for **3c** is not necessarily its most stable conformation.

Whereas bidentate ligands **2a-c** promote formation of a symmetric $[N\cdots C\cdots N]^+$ complex, or possibly a rapidly equilibrating pair of asymmetric $[N–C\cdots N]^+ \rightleftharpoons [N\cdots C–N]^+$ complexes,[52] the monodentate Lewis bases pyridine and picoline form asymmetric ion pairs with **1a** as indicated by the observation of two sets of ^{15}N NMR chemical shifts for **5b-c** (Table 1, Figure 3). The coordination shifts, $\Delta\delta^{15}N_{coord}$, of the latter complexes suggests that one nitrogen forms a strong, presumably covalent, bond to the carbenium carbon of **1a**, whereas the other nitrogen is involved in a weaker secondary interaction. This hypothesis was corroborated by the identification by single-crystal X-ray diffraction of 1-tritylpyridin-1-ium tetrafluoroborate crystals (CCDC 1581474), formed from the CD_2Cl_2 solution of **5c** (Figure 4). Hence, the bidentate Lewis

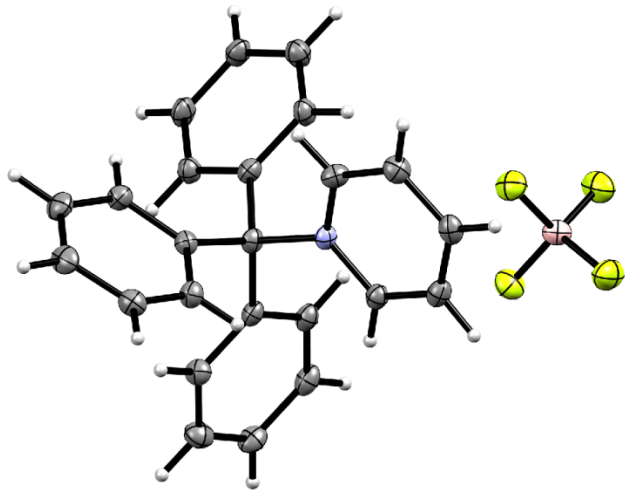

Figure 4. The molecular structure of 1-tritylpyridin-1-ium tetrafuloroborate. The thermal displacement parameters are shown at the 50% probability level.

base **2c** stabilizes the reactive carbenium ion **1a**, whereas its monodentate analogue, pyridine, undergoes *N*-alkylation with the electrophile. The δ^{15}N -144.0 ppm of **3c** indicates a strong N–C bond, which is close in chemical shift to that of the covalently functionalized pyridine of **5c** (δ^{15}N -153.3 ppm). Strong complexation for **3c** was supported by the comparable translational diffusion coefficients of **1a** (11.5×10^{-10} m^2s^{-1}) and **2c** (13.8×10^{-10} m^2s^{-1}) of the complex. The diffusion coefficients of **1a** and one of the pyridines ($\Delta\delta^{15}N_{coord}$ -86.3 ppm) of complex **5c** are similar (9.8×10^{-10} m^2s^{-1} and 9.4×10^{-10} m^2s^{-1}), indicating that these are connected, whereas the second weakly complexing pyridine ($\Delta\delta^{15}N_{coord}$ -8.8 ppm) has a diffusion coefficient ($25.6 \times 10^{-10}m^2$ s^{-1}) that indicates that this pyridine moves independently of **1a** in solution.

Dynamics. Compounds **3a-c** might be involved in a bell–clapper-type rearrangement;[38] that is, instead of being present as static and symmetric $[N\cdots C\cdots N]^+$ tetrel bond complexes, they might exist in solution as dynamic mixtures of rapidly exchanging complexes possessing a covalent C–N bond and a pyridine weakly connected through a conventional C···N tetrel bond, $[N–C\cdots N]^+ \rightleftharpoons [N\cdots C–N]^+$. To differentiate between the possibilities of a static and symmetric complex vs. a mixture of rapidly interconverting, weakly coordinating ones, we followed the standard procedures of the field,[38] acquiring ^{1}H and ^{13}C NMR and ^{1}H,^{15}N HMBC spectra for **3d** at various temperatures. Both the static and the dynamic geometries are expected to show a single sharp set of NMR signals at higher temperatures. A single set of signals is expected to remain detectable also at low temperature for a static $[N\cdots C\cdots N]^+$ tetrel bond complex, whereas for a dynamic mixture of asymmetric structures, two sets of signals, or at least significant signal broadening, is expected.[38] We observed a single sharp set of ^{1}H, ^{13}C and ^{15}N NMR signals at all temperatures, including at -40°C (Figure S3-S5, Supporting Information). This observation is best compatible with a static and symmetric geometry, even if it cannot fully exclude a very low barrier $[N–C\cdots N]^+ \rightleftharpoons [N\cdots C–N]^+$ interconversion, with an energy barrier $\Delta G^{\ddagger}$ << 38 kJ/mol and half-life of the possible interconverting states $t_{1/2}$ << 6.4 µs, when estimated from the chemical shift difference of pyridine (**4c**, $\delta(^{15}N)$ -67 ppm) and 1-tritylpyridinium ion (**5c**, $\delta(^{15}N)$ -153 ppm) as model compounds for the equally populated, not exchanging free vs. *N*-alkylated end states, the ^{15}N NMR observation frequency 50.67 MHz and a coalescence temperature < -40°C.[53] In order to detect a possible low-barrier interconversion, we further performed isotopic perturbation of equilibrium (IPE) NMR measurements.[54,55] Similar to earlier studies of related systems, we compared the temperature dependence of the secondary deuterium isotope effects of **3d** to those of a static reference, **2c**, and of its hydrogen bonded $[N–H\cdots N]^+ \rightleftharpoons [N\cdots H–N]^+$ complex used as a dynamic reference, as described in detail elsewhere.[15,18-21,56] Selective deuterium labelling of **2c** was performed at the pyridine carbon closest to the nitrogen,[19] and isotope effects were collected in the temperature range 25 °C to -40 °C, for all pyridine carbons. Signal overlaps prohibited us from determining the temperature dependence of three- and four-bond isotope effects, and hence from drawing a reliable conclusion from the IPE NMR study (for details see page S46-S48, in the Supporting Information). Overall, the variable temperature study suggest that **3** is expectably present in solution as a static and symmetric $[N\cdots C\cdots N]^+$ tetrel bond complex, however we cannot fully exclude the possibility of

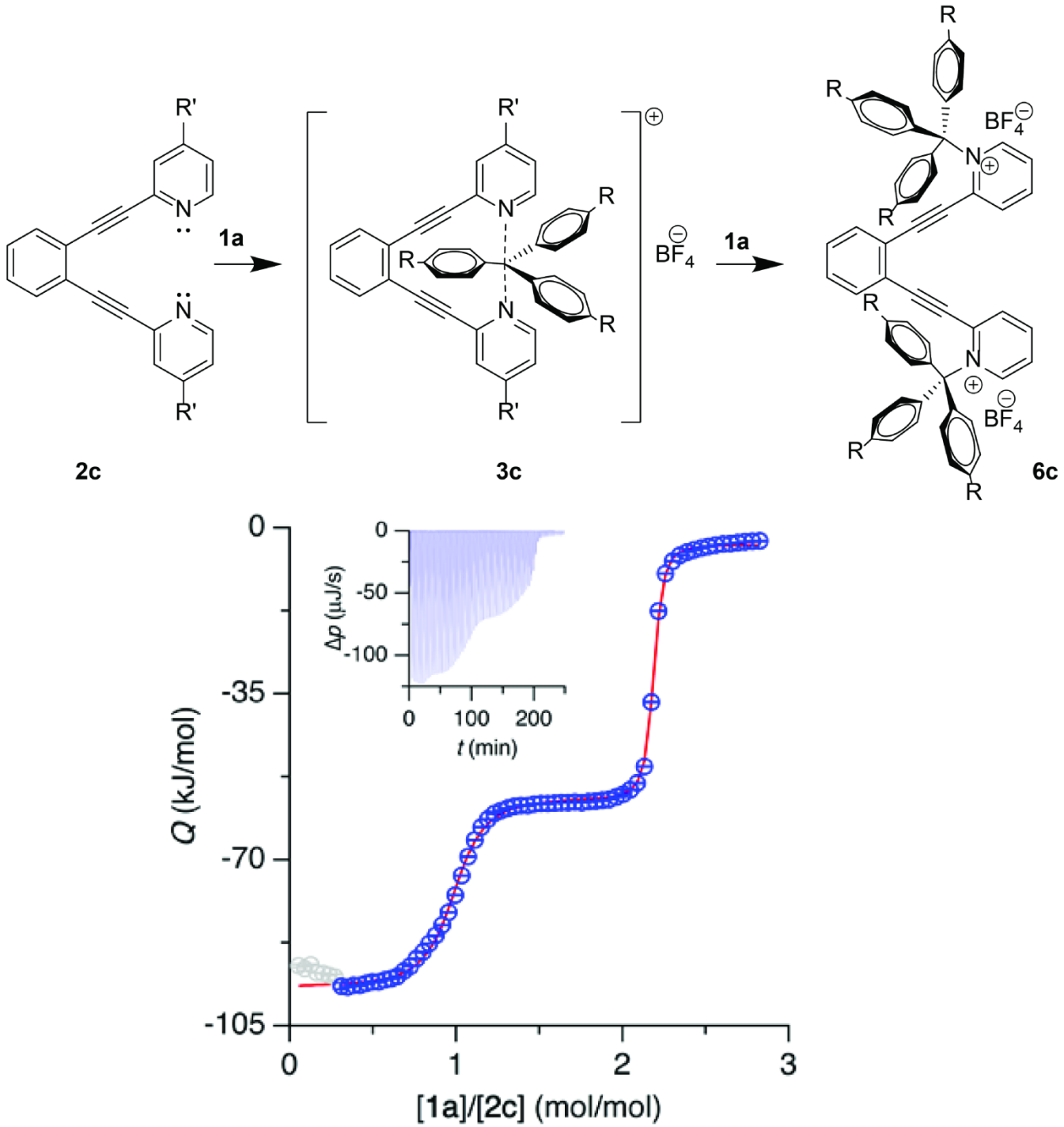

Figure 5. Titration of the bidentate ligand **2c** with **1a** yields the strong 1:1 complex, **3c** (top). Upon addition of an excess of **1a**, the 1:2 complex of **1a**:**2c**, **6c** is formed, as revealed by the bimodal shape of the isotherm (bottom). Isothermal titration calorimetry was performed at 25°C. Triphenylcarbenium tetrafluoroborate **1a** at a concentration of 6.6 mM was titrated to the bidentate ligand **2c** at a concentration of 0.5 mM. The main panel shows the isotherm depicting normalized heats of reaction, *Q*, as a function of the **1a**/**2c** molar ratio in the calorimeter cell (blue circles) along with uncertainties (blue horizontal lines) resulting from baseline assignment and peak integration.[57] Non-linear least-squares fits (red solid line) was based on the presumption of two interaction sites,[58] as reflected in the bimodal shape of the isotherm. Inset: The corresponding raw thermogram displaying differential heating power, Δ*p*, versus time, *t*. Best-fit parameter values and associated confidence intervals are summarized in the text, with the detailed analysis contained in the Supporting Information. Note that the structure drawn for **3c** is not necessarily its most stable conformation.

interconversion of analogous asymmetric $[N–C···N]^+ \rightleftharpoons [N···C–N]^+$ geometries encompassing conventional N–C covalent, and N···C tetrel bonds.

Despite repeated attempts, the crystallization of **3c** and **3d** remained unsuccessful. It should, however, be noted that X-ray crystallography would not necessarily be able to describe

the geometry of three-center tetrel bond complexes in solution. The analogous $[N–H–N]^+$ hydrogen bond complexes were shown to be a rapidly interconverting mixture of asymmetric geometries in solution whereas they are static, symmetric complexes in the solid state.[15] Preliminary DFT calculations of **5c** and **3c** were unable to reproduce the experimental observations (see Supporting Information S51–S66 for details). This may indicate the need for higher-level computational approaches or that our structural interpretation of the NMR data is not sufficiently accurate. DFT has previously correctly predicted the geometry of an analogous asymmetric, intramolecular three-center tetrel bond complex.[37] Continued experimental and computational investigations of the above and closely related molecular systems are expected to be capable of verifying or refuting the proposed structures of **3a–f**.

Binding affinity. Isothermal titration calorimetry was conducted to determine the binding strength of complex **3c**. Titration of the CH_2Cl_2 solution of **2c** with triphenyl carbenium tetrafluoroborate, **1a**, dissolved in CH_2Cl_2, indicates the formation of a strong 1:1 complex characterized by K_1 = 1.9 nM, $\Delta G°_1$ = -49.8 kJ/mol, $\Delta H°_1$ = -93.4 kJ/mol, and $-T\Delta S°_1$ = 43.7 kJ/mol. Upon addition of an excess of **1a**, a 1:2 (**2c**/**1a**) complex **6c** is generated in a second, weaker binding step with K_2 = 237 nM, $\Delta G°_2$ = -37.8 kJ/mol, $\Delta H°_2$ = -53.1 kJ/mol, and $-T\Delta S°_2$ = 15.3 kJ/mol (Figure 5). Formation of the latter dialkylated **6c** is in line with the smooth reaction of pyridine with triphenylcarbenium tetrafluoroborate, **1a**, to form 1-tritylpyridin-1-ium tetrafluoroborate (**5c**). In the doubly positively charged complex **6c**, the charge of the carbenium is presumably distributed over the entire conjugated aromatic system, akin to the analogous halogen bonded complexes.[19,21] The formation of **6c** upon addition of an excess of **1a** to **2c** was also confirmed by NMR (δ^{15}N -143.7 ppm, Supporting Information, Figure S6). The free energy $\Delta G°_1$ of the initial complex formation results from a remarkable enthalpic contribution, which is partly offset by a substantial loss of entropy; for **6c**, both contributions are largely reduced in magnitude, but the reaction remains purely enthalpy driven. A reverse titration, that is, addition of a CH_2Cl_2 solution of **2c** into the solution of **1a**, supported the above binding model (Supporting Information).

Electron density. Upon complexation, a considerable deshielding of the nitrogen of **2a-c** and shielding of the carbenium carbon of **1a-f** were observed. The magnitude of the observed chemical shift changes (Table 1) are expected to reflect the electron density alteration of the studied complexes, even if they do not necessarily correlate with bond strength.[21] Upon decreasing the electron deficiency of the carbenium carbon, **3c→f**, smaller $\Delta\delta^{15}N_{coord}$ and $\Delta\delta^{13}C_{coord}$ are detected (Table 1). This may be due to a gradual weakening of the $[N\cdots C\cdots N]^+$ tetrel bond interaction upon decreasing the electrophilicity of the carbenium carbon.

Increasing electron density of the Lewis basic nitrogen of the bidentate ligand, **2a** < **2c** < **2b**, is associated with an increase of $\Delta\delta^{15}N_{coord}$, in the order **3a** < **3c** < **3b**. In contrast, $\Delta\delta^{13}C_{coord}$ remains virtually unaltered. The weak electron donating effect of a 4-Me substituent does not have a vast influence on the coordination shifts as reflected by the comparable $\Delta\delta^{15}N_{coord}$ and $\Delta\delta^{13}C_{coord}$, of **3b** and **3c** as well as **5b** and **5c**.

Masking Lewis acidity by tetrel bond formation. Triphenyl carbenium ions are powerful Lewis acid catalysts that

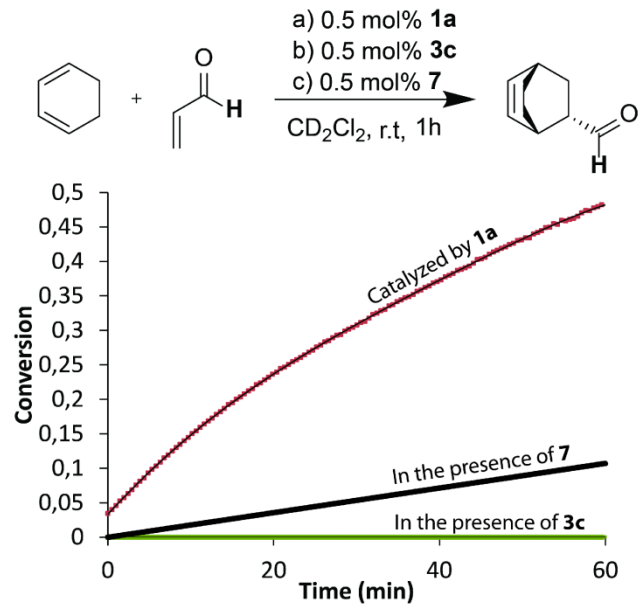

Figure 6. The progress of the Diels–Alder condensation, run under literature conditions,[59] of 1,3-cyclohexadiene (1.2 eq) and acrolein (1 mmol) in CD_2Cl_2 in the presence of 0.5 mol% **1a** or **3a** was monitored by ^{1}H NMR in an NMR tube at 25 °C for 1 hour. The integral of the signals of the aldehyde proton of the starting material and of the product was used to follow the progress of the reaction. Whereas the reaction catalyzed by **1a** (red) progresses with a second order rate, the addition of **2c** inhibits it (green) through masking the Lewis acidic **1a** by formation of the tetrel bond complex **3c**.

were used, for example, to facilitate Diels–Alder reactions.[59] Such reactions do not proceed in the absence of a catalyst, whilst upon activation with 0.5 mol% triphenylcarbenium ion, they give high conversion within 30 min. To provide additional evidence for the participation of the carbenium p-orbital in a tetrel bond, involving an orbital interaction, we ran the Diels–Alder condensation of acrolein and cyclohexadiene (Figure 6) in the presence of **1a**, **3c** and **7**. Here, **7** denotes 2-((2-(phenylethynyl)phenyl)ethynyl)-1-tritylpyridin-1-ium, formed upon mixing **1a** and 2-((2-(phenylethynyl)phenyl)-ethynyl)pyridine (Supporting Information, page S8), a mononitrogen analogue of **3c**. We monitored the progress of each reaction by acquiring the ^{1}H NMR integrals of the starting material and the product using their well-separated aldehyde protons as reporter nuclei. As shown in Figure 6, the Diels–Alder reaction progresses with second order rate in the presence of **1a**, whereas it does not give any conversion in the presence of **3c** and only low conversion in the presence of **7**. This is in excellent agreement with the observation of Franzen, reporting that addition of the *N*-Lewis base 2,6-di-tert-butylpyridine to **1a** inhibits the Diels-Alder catalytic activity of the latter.[59] The lack of catalytic activity of **3c** substantiates strong complexation of **1a** to **2c** by the masking of the Lewis acidic empty p-orbital of **1a** without, however, providing evidence specifically for formation of a three-center four-electron bond. The observation is in agreement with the outcome of the NMR and isothermal titration calorimetric studies, and thus with formation of a stable intermolecular complex.

CONCLUSIONS

The first experimental evidence of a stable, intermolecular three-center four-electron tetrel bond complex is presented. We demonstrate that a carbenium ion is converted into a tetrel

bond complex by simultaneous overlap of both lobes of the empty p-orbital of the former species with the nonbonding orbitals of two Lewis bases positioned to form a linear three-center four-electron $[N–C–N]^+$ bond. This bond resembles the analogous three-center $[N–I–N]^+$ halogen bond[22] in geometry and energy. Thus, formation of the $[N–C–N]^+$ complex is associated with ~50 kJ/mol change in free energy, as detected by isothermal titration calorimetry. This complex possesses by far the strongest tetrel bond so far reported.[60,61] Its high stability is corroborated by the inability of the complex to act as a Lewis acid catalyst in a Diels–Alder reaction at room temperature. The observation of a single set of NMR signals even at low temperatures suggests that the complex has a symmetric three-center four electron bond, whose electron density can be modulated by substitution. However, our observations cannot fully exclude a very low barrier interconversion of asymmetric species in solution. It should be noted that we were unable to confirm the symmetric $[N–C–N]^+$ geometry by computation on the DFT level. Further computational studies of the complexes studied herein may thus provide critical insights for theoretical chemistry and, possibly, a more accurate structural interpretation of the NMR and ITC data of **3a-f**.

The formation of a stable three-center four-electron tetrel bond complex requires the involvement of a bidentate Lewis base whose donors are positioned at an optimal distance and geometry to promote simultaneous overlaps with the unfilled p-orbital of a carbenium ion. Upon use of two equivalents of an analogous monodentate Lewis base, the carbenium does not form a stable bidentate complex but rather *N*-alkylates the electron donor. It should be noted that the isoelectronic $[bis(pyridine)iodine]^+$ and $[bis(pyridine)bromine]^+$-type halogen bonded model systems are stable in solution.[19,20,22] Thus, in contrast with the $[N–C–N]^+$ complexes, the $[N–X–N]^+$ ones do not require the use of a bidentate ligand for thermodynamic stability, highlighting an intriguing difference between halogen and tetrel bonding. The difference in tetrel, halogen and hydrogen bonding is further demonstrated by the fact that $[N–C–N]^+$ and $[N–I–N]^+$ complexes are strong, static and symmetric, whereas the analogous $[N–H–N]^+$ complexes are present in solution as mixtures of rapidly interconverting asymmetric tautomers, $[N–H\cdots N]^+ \rightleftharpoons [N\cdots H–N]^+$, and lack extra stabilization.[15,17] Despite its fundamental importance, the three-center four-electron bond responsible for the stability of **3a-f** remains an unsolved challenge for bonding theories.[45] Its further investigation is expected to provide critical insights in numerous fields, not least in synthetic and theoretical chemistry.

The structure of **3a-f** resembles the transition state geometry of the S_N2 reaction,[44] with the position of the Lewis bases and the carbonium carbon corresponding to that of the linearly arranged nucleophile, the central carbon and the leaving group in the latter. Similar to the S_N2 transition state, the central carbon of these complexes forms a three-center four electron bond within a trigonal bipyramidal geometry. Therefore, these compounds may be superior model systems for the S_N2 transition state as compared with the previously proposed, isoelectronic three-center four-electron halogen bonds.[23,44] Compounds **3a-f** are thermodynamically stable at room temperature in solution, and are easily modifiable through simple synthetic transformations. By an independent variation of the electron density of the apically positioned Lewis bases, the geometry of the $[N–C–N]^+$ complex ought to be adjustable to reflect various stages of the S_N2 reaction. Hence, the presented tetrel bond complexes and their close analogues are expected to be applicable to gain further insights into fundamental reaction mechanisms and chemical bonding theories.

ASSOCIATED CONTENT

Supporting Information. Details on the synthesis, spectroscopic data for compound identification, and details on the NMR, computational, X-ray diffractometric, and kinetic investigations. This material is available free of charge via the Internet at http://pubs.acs.org.s.

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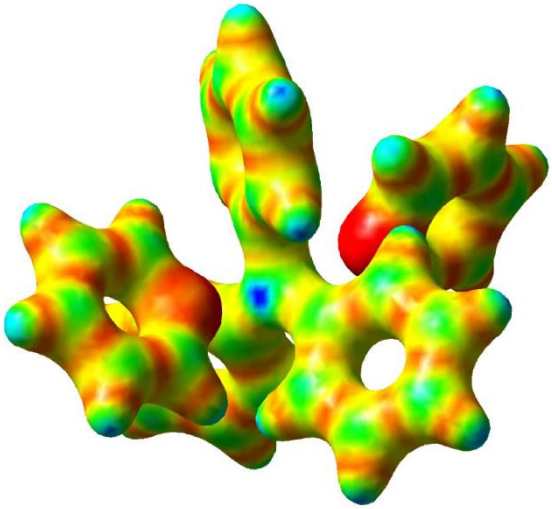
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